# Synthesis of a Sulfonated Two-Dimensional Covalent Organic Framework as an Efficient Solid Acid Catalyst for Biobased Chemical Conversion

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Because of limited framework stability tolerance, de novo synthesis of sulfonated covalent organic frameworks (COFs) remains challenging and unexplored. Herein, a sulfonated twodimensional crystalline COF, termed TFP-DABA, was synthesized directly from 1,3,5-triformylphloroglucinol and 2,5-diaminobenzenesulfonic acid through a previously reported Schiff base condensation reaction, followed by irreversible enol-toketo tautomerization, which strengthened its structural stability. TFP-DABA is a highly efficient solid acid catalyst for fructose conversion with remarkable yields (97% for 5-hydroxymethylfurfural and 65% for 2,5-diformylfuran), good chemoselectivity, and good recyclability. The present study sheds light on the de novo synthesis of sulfonated COFs as novel solid acid catalysts for biobased chemical conversion.

Covalent organic frameworks (COFs) are porous crystalline polymers constructed from organic building blocks by using reticular chemistry.<sup>[1]</sup> Because of their features, such as periodic architectures, low densities, and permanent porosities, they have been widely investigated for various applications, such as gas storage/separation,<sup>[2]</sup> catalysis,<sup>[3]</sup> and optoelectronics.<sup>[4]</sup> COFs can serve as ideal heterogeneous catalysts due to their uniform yet tunable porosity and rich functionality, and are capable of reaching excellent catalytic activity and selectivity values that are superior to their homogeneous analogues. In principle, catalytically active COFs can be constructed from direct or indirect strategies that are widely employed in preparing heterogeneous catalysts.<sup>[5]</sup> Most of the reported catalytically active COFs are prepared through indirect strategies, such as postmodification or immobilization with other catalytically active species.<sup>[3a-f]</sup> Because of the limited framework stability tolerance towards catalytically active functional groups (e.g., acid or basic groups), the direct strategy (or de novo synthesis)

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by using molecular catalysts (precatalysts) as building blocks to prepare catalytically active COFs remains limited.  $^{\rm [3g,h]}$ 

The use of renewable biomass resources (e.g., fructose, glucose, cellulose, starch, etc.) in biobased chemical synthesis through chemical conversion is of great significance, not only for basic science, but also to relieve growing concerns with regard to the exhaustion of fossil fuels and deterioration of our environment.<sup>[6]</sup> As a versatile and key scaffold for biorefineries, 5-hydroxymethylfurfural (HMF) has a huge potential in downstream applications, such as fuels and fine chemicals.<sup>[7]</sup> Currently, HMF is mainly synthesized from biobased hexose sugars through acid-promoted dehydration.<sup>[8]</sup> Several sulfonic acid derived homo- and heterogeneous catalysts have been developed for this process.<sup>[9]</sup> Challenges to homogeneous catalysts include product separation and equipment corrosion, whereas heterogeneous catalysts normally suffer from problems of low catalytic performance and long reaction times. Therefore, the design of highly efficient solid acid catalysts is still of paramount importance for this conversion.

Banerjee et al. demonstrated remarkable chemical stabilities of COFs obtained through irreversible enol-to-keto tautomerization.<sup>[10]</sup> Inspired by their findings, herein we report the de novo synthesis of a sulfonated 2D COF named TFP-DABA. TFP-DABA was prepared by the Schiff base condensation reaction between 1,3,5-triformylphloroglucinol (TFP) and 2,5-diaminobenzenesulfonic acid (DABA), followed by irreversible enolto-keto tautomerization, which locked it into a more stable isomorph that was compatible with the sulfonic acid groups (Scheme 1). TFP-DABA was studied as a solid acid catalyst in fructose dehydration to HMF, or 2,5-diformylfuran (DFF), when KBr was used as a cocatalyst; it exhibited remarkable yields (97% for HMF and 65% for DFF), good chemoselectivity, and good recyclability.

A suspension of TFP and DABA in a 10:1 (*v*/*v*) mixture of mesitylene/dioxane (1:4) and aqueous acetic acid (3 M) was heated at 100 °C for 3 days to give TFP-DABA as a red crystalline solid in 86% yield (see the Experimental Section). TFP-DABA was insoluble in water and common organic solvents and was formulated to be  $C_{12}H_8N_2O_5S$  based on elemental analysis performed on a guest-free sample. FTIR spectra of TFP-DABA indicated the disappearance of the carbonyl stretching band of TFP ( $\tilde{v} = 1643 \text{ cm}^{-1}$ ) accompanied by a series of new characteristic stretching bands observed at  $\tilde{v} = 1578$  and 1238 cm<sup>-1</sup> arising from the C=C and C–N stretching bands, respectively (Figure S1a in the Supporting Information). The bands observed at  $\tilde{v} = 1026$  and 1080 cm<sup>-1</sup>, along with





Scheme 1. Synthetic scheme for the preparation of TFP-DABA by Schiff base condensation and enol-to-keto tautomerization (cavity size considering van der Waals radius is indicated).

**Communications** Thermogravimetric analysis (TGA) reveals that TFP-DABA is thermally stable up to 250°C (Figure S4 in the Supporting Information). Field-emission (FE) SEM images show that TFP-DABA crystallized in a uniform

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SEM images show that TFP-DABA crystallized in a uniform block-shaped morphology with dimensions ranging from 50 to 100 nm (Figure S5 in the Supporting Information). The permanent porosity of TFP-DABA was confirmed by N<sub>2</sub> sorption isotherms at 77 K (Figure 2). The activated sample exhibits a typical type IV isotherm, with a pore volume of  $0.48 \text{ cm}^3 \text{g}^{-1}$ and surface BET а area of 158.6  $m^2 g^{-1}$  (272.7  $m^2 g^{-1}$  based on the Langmuir model). The hysteresis between adsorption and desorption branches may come from the interstitial voids among the COF nanoparticles.<sup>[12]</sup> The smallest pore size of TFP-

a shoulder at  $\tilde{\nu} = 1438 \text{ cm}^{-1}$ , can be attributed to the O=S=O symmetric and asymmetric stretching bands, which indicate the existence of the sulfonic acid group. The amount of dangling sulfonic acid groups in TFP-DABA was estimated to be  $3.15 \text{ mmolg}^{-1}$  by acid-base titration, which was comparable to the theoretical value of  $3.42 \text{ mmolg}^{-1}$  and confirmed almost full accessibility of these groups. The structure of TFP-DABA was further confirmed by <sup>13</sup>C cross-polarization magic-angle-spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy; the characteristic chemical shift at  $\delta = 182.1 \text{ ppm}$  was attributed to the carbonyl carbon (Figure S2 in the Supporting Information). The results of FTIR and CP/MAS NMR spectroscopy are similar to previous studies, which confirms enol-to-keto tautomerization in TFP-DABA.<sup>[10]</sup>

The crystallinity of TFP-DABA was determined by powder Xray diffraction (PXRD) analysis (Figure 1). Based on the hexagonal P6 (no.174) space group, two possible structural models with eclipsed and staggered 2D stacking were built by using the Materials Studio software package.<sup>[11]</sup> The experimental PXRD pattern of TFP-DABA matches well with the simulated pattern obtained by using the eclipsed 2D stacking model and contains no diffraction peaks that could be attributed to starting materials (Figure S3 in the Supporting Information). Two sharp peaks at 4.7 and 16.3° were observed in the experimental PXRD pattern of TFP-DABA; these corresponded to the reflection from the (100) and (001) planes, respectively. The slightly broad peak at higher  $2\theta$  angles may be attributed to defects in the  $\pi$ - $\pi$  stacking between successive COF layers.<sup>[10c]</sup> After geometrical energy minimization by using the universal force field, the unit cell parameters of TFP-DABA were calculated to be a = b = 22.90 Å and c = 5.47 Å.

DABA calculated by using nonlocal density functional theory (NLDFT) was 13.8 Å, which was quite close to the pore size of



**Figure 1.** a) Crystal structure of TFP-DABA, assuming 2D eclipsed stacking viewed through [001] (left) and [100] (right) directions along with the interlayer distance; b) simulated and experimental PXRD patterns of TFP-DABA.



Figure 2. Nitrogen sorption isotherms (77 K) and pore size distribution (inset) of TFP-DABA.

1.4 nm measured from the predicted crystal structure (Scheme 1).

The presence of 1D microporous channels and easily accessible sulfonic acid groups in TFP-DABA prompted us to explore its application as a solid acid catalyst for fructose dehydration. Our initial studies identified TFP-DABA as an effective catalyst for the dehydration of fructose into HMF and a variety of reaction conditions were then screened. The screening of reaction temperature was conducted by using dimethyl sulfoxide (DMSO) as solvent with 5 mol% loading of TFP-DABA as a catalyst. We found that 100 °C was the most suitable temperature for this reaction to afford a high yield of HMF (65%) and good chemoselectivity (97%; Table 1, entries 1–4). Increasing the catalyst loading from 5 to 10 mol% led to better yields of HMF (up to 97%) with similar chemoselectivity (Table 1, entries 2, 5, and 6). For comparison, when the monomer DABA was used as a catalyst under similar conditions, full fructose conversion

Table 1. Synthesis of HMF from fructose catalyzed by TFP-DABA. $HOH_2C$ $OH$ $OH$ $CH_2OH$ $OH$							
Entry <sup>[a]</sup>	TFP-DABA	Т	Fructose	HMF	:		
	loading [mol %]	[°C]	conversion [%]	selectivity [%]	yield [%]		
1	5	80	42	97	41		
2	5	100	67	97	65		
3	5	120	88	90	79		
4	5	140	>99	80	80		
5	7.5	100	84	97	81		
6	10	100	>99	97	97		
7 <sup>[b]</sup>	-	100	>99	54	54		
8	-	100	5	n.d. <sup>[c]</sup>	n.d. <sup>[c]</sup>		
9 <sup>[d]</sup>	10	100	>99	95	95		
10 <sup>[e]</sup>	10	100	>99	94, 95, 94	94, 95, 94		
11 <sup>[e]</sup>	5	100	66, 64, 61	97, 95, 97	64, 61, 59		
[a] On a 0.28 mmol scale, see the Experimental Section for details.							

[d] On a 3 mmol scale. [e] Recycled TFP-DABA was used as the catalyst for one to three cycles, respectively.

could still be achieved, but with only 54% yield of HMF (Table 1, entry 7); this indicated that TFP-DABA was more active and chemoselective than its homogeneous counterpart. A control experiment without catalyst revealed that only 5% fructose conversion was achieved, without any detectable HMF as the product (Table 1, entry 8). Furthermore, when a scaledup amount of fructose (tenfold) was employed with TFP-DABA as the catalyst, full fructose conversion with 95% yield of HMF were still attained (Table 1, entry 9). These results reveal that TFP-DABA is a highly efficient catalyst for the dehydration of fructose into HMF. To the best of our knowledge, TFP-DABA is among the best solid acid catalysts for this transformation reported so far.<sup>[8c]</sup> It needs to be pointed out that, although water has been proposed as the green solvent of choice for many biomass-conversion reactions,<sup>[7a,8b]</sup> no catalytic activity was observed in our study with water as the solvent. This is probably because of the instability of HMF in water.<sup>[13]</sup>

We then examined the heterogeneity and recyclability of TFP-DABA. The supernatant of the reaction media obtained by using a regular filter during the dehydration reaction process did not afford any additional product; this indicates the role of heterogeneous catalyst played by TFP-DABA. Upon completion of the reaction, TFP-DABA could be recovered in quantitative yield and used repeatedly without significant loss of its catalytic activity for the following three runs (full fructose conversions with 94, 95, and 94% yield of HMF for 1-3 runs, respectively; Table 1, entry 10). Moreover, to avoid the excess use of TFP-DABA, we also recycled and reused the catalyst before equilibrium conversion (Table 1, entry 2); 66, 64, and 61% fructose conversions with 64, 61, and 59% yield of HMF could be obtained for 1-3 runs, respectively (Table 1, entry 11). The FTIR spectrum of recycled TFP-DABA remained the same as that of the original one (Figure S1b in the Supporting Information). Moreover, the supernatant of the reaction media did not contain any monomers (TFP or DABA) of TFP-DABA, which indicated its structural integrity during catalysis. Recycled TFP-DABA lost its crystallinity after three runs, as revealed by the PXRD patterns (Figure S6 in the Supporting Information). This might due to the partial exfoliation of 2D COF material; this was also observed in a previous study.<sup>[3c]</sup> However, the short-range chemical bonding and composition of TFP-DABA should remain unchanged. We found that the crystallinity of recycled TFP-DABA could be easily reconverted by subjecting it to the initial synthetic conditions, as confirmed by the PXRD and BET profiles of recrystallized TFP-DABA (Figures S6 and S7 in the Supporting Information). Although without crystallinity after three runs, TFP-DABA still remained a solid that could be recovered through centrifugation.

To further study the catalytic performance of TFP-DABA and its homogeneous counterpart DABA, kinetic studies for fructose dehydration were carried out by using a 10 mol% loading of TFP-DABA or DABA in DMSO at 100 °C (Figure 3). When DABA was used as the catalyst, full fructose conversion was obtained within 10 min, although the desired yield of HMF was moderate (70%) and then decreased to 54% after 1 h due to side reactions. In contrast, TFP-DABA displayed remarkably enhanced catalytic activity and chemoselectivity, with the fruc-



Figure 3. Kinetic study of fructose dehydration catalyzed by TFP-DABA (blue) and DABA (red). Reaction conditions: fructose (50 mg), catalyst (10 mol%), DMSO (1 mL), 100  $^{\circ}$ C.

tose conversion and HMF yield increasing steadily towards 100 and 97%, respectively, in 1 h. It is clear that, compared with its homogeneous analogue, TFP-DABA exhibited slower reaction kinetics possibly due to slow mass diffusion within the porous framework. The enhanced catalytic activity of TFP-DABA may originate from the increased acidity of sulfonic acid groups owing to the  $\pi$ -extended network of TFP-DABA.<sup>[14]</sup>

Next, we further expanded TFP-DABA to another biobased chemical synthesis. Although HMF has been widely explored as a versatile synthetic intermediate for fine chemicals, its application is largely limited by the low stability. This shortcoming can be overcome by oxidizing HMF to DFF, which is another important and more stable platform molecule.<sup>[6,7,15]</sup> Great efforts have been made for this transformation, although only low yields of DFF are obtained that rarely exceed 60%.<sup>[16]</sup> Recently, Laugel et al. reported a one-pot synthesis of DFF from fructose with NaBr as a catalyst in DMSO under a high temperature of 150 °C.<sup>[16d]</sup> To demonstrate the applicability of TFP-DABA as a solid acid catalyst, we adopted a similar protocol for the one-pot synthesis of DFF from fructose directly under the catalysis of TFP-DABA and KBr. As shown in Scheme 2, with the help of a 10 mol% loading of TFP-DABA



Scheme 2. One-pot synthesis of DFF from fructose catalyzed by TFP-DABA and KBr.

and 20 mol% loading of KBr, fructose could be directly converted into DFF in 65% yield with full conversion after 12 h under a lower temperature of 100 °C at atmospheric pressure. Without TFP-DABA and only a 20 mol% loading of KBr, no DFF was observed under the identified conditions. Moreover, there was a minimal impact on DFF yield when this transformation was conducted under a high-pressure oxygen environment (5 bar; 1 bar= $1 \times 10^5$  Pa). Therefore, we speculated that this

transformation should occur through the formation of 5-(bromomethyl)furan-2-carbaldehyde, followed by a Kornblum-type reaction, with the help of the association of TFP-DABA with bromide salts, which was similar to the previous study disclosed by Laugel et al.<sup>[16d]</sup> As far as we know, this catalytic performance is comparable to the best results reported so far for such a conversion.<sup>[16c]</sup>

In conclusion, we presented the de novo synthesis of a sulfonated COF TFP-DABA, which exhibited excellent catalytic activity and chemoselectivity for the conversion of fructose into HMF and DFF. Our study paves a solid way towards the de novo synthesis of catalytically active COFs and their applications in biobased chemical conversion.

## **Experimental Section**

#### Synthesis of TFP-DABA

A 10 mL Pyrex tube was charged with TFP (21.0 mg, 0.1 mmol), DABA (28.2 mg, 0.15 mmol), mesitylene/dioxane (1:4 v/v, 1 mL), and aqueous acetic acid (0.1 mL, 3 M). The mixture was stirred for 10 min to give a homogenous suspension. The tube was then flash frozen at 77 K by using a liquid nitrogen bath and degassed by three freeze–pump–thaw cycles, sealed under vacuum, and then heated at 100 °C for 3 days. A red precipitate formed and was collected by centrifugation, washed with anhydrous DMF, anhydrous CH<sub>2</sub>Cl<sub>2</sub>, anhydrous THF, and anhydrous acetone. The washed sample was then solvent-exchanged with anhydrous methanol 2–3 times and dried at 150 °C under vacuum for 12 h to give a deepred powder in 86% yield. Elemental analysis calcd (%) for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>S: C 49.31, H 2.76, N 9.58, S 10.97; found: C 49.94, H 2.70, N 9.06, S 11.26.

#### Fructose conversion into HMF

In a typical run, fructose (50 mg), TFP-DABA (8 mg, 10 mol%), and DMSO (1 mL) were added to a 10 mL Pyrex tube. The tube was purged with argon, sealed, and then placed in a preheated oil bath at 100 °C with vigorous stirring for 1 h. The reaction was stopped by quenching the tube in an ice bath at 0 °C. The mixture was filtered and then decanted into a volumetric flask with water as diluent. The products were analyzed by HPLC.

#### Fructose conversion into DFF

In a typical procedure, fructose (50 mg), TFP-DABA (8 mg, 10 mol%), KBr (7 mg, 20 mol%), and DMSO (1 mL) were added to a 10 mL Pyrex tube. After sealing, the tube was placed in a preheated oil bath at 100 °C with vigorous stirring for 12 h. The reaction was stopped by quenching the tube in an ice bath at 0 °C. The mixture was filtered and then decanted into a volumetric flask with water as the diluent. The products were analyzed by HPLC.

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